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1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY DTIC ELECTED JUN 04 1990			3 DISTRIBUTION/AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited.		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
4 PERFORMING ORGANIZATION REPORT NUMBER ONR-TR 16			7a NAME OF MONITORING ORGANIZATION Office of Naval Research Chemistry Division		
6a NAME OF PERFORMING ORGANIZATION Naval Ocean Systems Center		6b OFFICE SYMBOL (If applicable)	7b ADDRESS (City, State, and ZIP Code) Arlington, VA 22217		
6c ADDRESS (City, State, and ZIP Code) Code 521 San Diego, CA 92152		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N0001490WX24290			
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (If applicable)	10 SOURCE OF FUNDING NUMBERS		
8c ADDRESS (City, State, and ZIP Code) Chemistry Division Arlington, VA 22217		PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
11 TITLE (Include Security Classification) Bimanes (1,5-Diazabicyclo(3.3.0)octadiendiones). Laser Activity in syn-Bimanes (UNCLASSIFIED)					
12 PERSONAL AUTHOR(S) E. D. Stevens, J. H. Eoyer, C. M. Lau, I. R. Politzer, K. Tangaraj, G. Kumar, V. T. Ramakrishnan, T. G. Pavlopoulos					
13a TYPE OF REPORT Interim Technical		13b TIME COVERED FROM 6/01/89 TO 5/31/90		14 DATE OF REPORT (Year, Month, Day) 23 Mar 1990	
15 PAGE COUNT					
16 SUPPLEMENTARY NOTATION Heteroatom Chemistry 1, 195-207 (1990).					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Syn-Bimanes, Laser activity, synthesis of syn-bimanes, spectroscopic and laser action properties of syn-bimanes,		
19 ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>The conversion of 3-methyl-4-benzyl-4-chloro-2-pyrazolin-5-one <u>10b</u> was catalyzed by a mixture of potassium fluoride and alumina to give syn-(methyl,benzyl)bi-mane <u>6</u> (62%) without detectable formation of the anti isomer <u>A6</u> [a 1:1 mixture (87%) of the isomers <u>6</u> and <u>A6</u> was obtained when the catalyst was potassium carbonate]. In a similar reaction syn-(methyl,carboethoxymethyl)bimane <u>7</u> (15%) with the anti isomer <u>A7</u> (36%) was obtained from 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one <u>10c</u>. syn-(Methyl, <math>\beta</math>-acetoxyethyl)bimane <u>8</u> (70%) was obtained from 3-methyl-4-<math>\beta</math>-acetoxyethyl-4-chloro-2-pyrazolin-5-one <u>10d</u> (potassium carbonate catalysis) and was convert-</p>					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a NAME OF RESPONSIBLE INDIVIDUAL Theodore G. Pavlopoulos			22b TELEPHONE (Include Area Code) (619) 553-2792		22c OFFICE SYMBOL

DD Form 147, 1-75

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S/N 0102-17-014-6603

SECURITY CLASSIFICATION OF THIS PAGE

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## 19 ABSTRACT cont.

ed by hydrolysis to *syn*-(methyl, $\beta$ -hydroxyethyl)bimane 9 (40%). Acetyl nitrate (nitric acid in acetic anhydride) converted *anti*-(amino,hydrogen)bimane 11 to *anti*-(amino,nitro)bimane 15 (91%), *anti*-(methyl,hydrogen)bimane 13 to *anti*-(methyl,nitro)(methyl,hydrogen)bimane 16 (57%), and degraded *syn*-(methyl,hydrogen)bimane 12 to an intractable mixture. Treatment with trimethyl phosphite converted *syn*-(bromomethyl,methyl)bimane 17 to *syn*-(dimethoxyphosphinylmethyl,methyl)bimane 18 (78%) that was further converted to *syn*-(styryl,methyl)bimane 19 (29%) in a condensation reaction with benzaldehyde. Treatment with acryloyl chloride converted *syn*-(hydroxymethyl,methyl)bimane 20 to its acrylate ester 21 (22%). Stoichiometric bromination of *syn*-(methyl,methyl)bimane 1 gave a monobromo derivative that was converted *in situ* by treatment with potassium acetate to *syn*-(acetoxymethyl,methyl)(methyl,methyl)bimane 47. *N*-Amino- $\mu$ -amino-*syn*-(methylene, methyl)bimane 24 (68%) was obtained from a reaction between the dibromide 17 and hydrazine. Derivatives of the hydrazine 24 included a perchlorate salt and a hydrazone 25 derived from acetone. Dehydrogenation of *syn*-(tetramethylene)bimane 26 by treatment with dichlorodicyanobenzoquinone (DDQ) gave *syn*-(benzo,tetramethylene)bimane 27 (58%) and *syn*-(benzo)bimane 28 (29%). Bromination of the bimane 26 gave a dibromide 29 (92%) that was also converted by treatment with DDQ to *syn*-(benzo)bimane 28. Treatment with palladium (10%) on charcoal dehydrogenated 5,6,10,11-tetrahydro-7*H*,9*H*-benz[6,7]indazol[1,2-*a*]benz[*g*]indazol-7,9-dione 35 to *syn*-( $\alpha$ -naphtho)bimane 36 (71%). The bimane 35 was prepared from 1,2,3,4-tetrahydro-1-oxo-2-naphthoate 37 by stepwise treatment with hydrazine to give 1,2,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one 38, followed by chlorine to give 3*a*-chloro-2,3*a*,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one 39, and base. Dehydrogenation over palladium converted the indazolone 34 to 1*H*-benz[*g*]indazol-3-ol 36. Helicity for the hexacyclic *syn*-( $\alpha$ -naphtho)bimane 36 was confirmed by an analysis based on molecular modeling.

The relative efficiencies (RE) for laser activity in the spectral region 500–530 nm was obtained for 37 *syn*-bimanes by reference to coumarin 30 (RE 100): RE > 80 for *syn*-bimanes 3, 5, 18, and  $\mu$ -(dicarbomethoxy)methylene-*syn*-(methylene,methyl)bimane 50; RE 20–80: for *syn*-bimanes 1, 2, 4, 20, 24, 26, and  $\mu$ -thia-*syn*-(methylene,methyl)bimane 50; and RE 0–20 for 26 *syn*-bimanes. The bimane dyes tended to be more photostable and more water soluble than coumarin 30. The diphosphonate 18 in dioxane showed laser activity at 438 nm and in water at 514 nm. Presumably helicity, that was demonstrated by molecular modeling, brought about a low fluorescence intensity for *syn*-( $\alpha$ -naphtho)bimane 36,  $\Phi$  0.1, considerably lower than obtained for *syn*-(benzo)bimane 28,  $\Phi$  0.9.

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Contract N001490WX24290

R&T Code 4131011---05

Technical Report No. 16

Bimanes (1,5-Diazabicyclo(3.3.0)octadiendiones). Laser Activity in  
syn-Bimanes

by

E. D. Stevens, J. H. Boyer, C. M. Lau, I. R. Politzer, K. Thangaraj,  
G. Kumar, V. T. Ramakrishnan, and T. G. Pavlopoulos

Prepared for Publication

in the

Heteroatom Chemistry 1, 195-207 (1990)

Naval Ocean Systems Center  
San Diego, CA 92152

24 May 1990

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Bimanes (1,5-Diazabicyclo[3.3.0]octadiendiones). Laser Activity in *syn*-Bimanes.

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GOVINDARAJULU KUMAR,<sup>a</sup> VAYALAKKAVOOR T. RAMAKRISHNAN,<sup>a</sup> EDWIN  
D. STEVENS,<sup>a</sup> JOSEPH H. BOYER,<sup>a\*</sup> and THEODORE G. PAVLOPOULOS<sup>c</sup>

Received \_\_\_\_\_.

**Abstract.** The conversion of 3-methyl-4-benzyl-4-chloro-2-pyrazolin-5-one 10b was catalyzed by a mixture of potassium fluoride and alumina to give *syn*-(methyl,benzyl)bi-mane 6 (62%) without detectable formation of the *anti* isomer A6 [a 1:1 mixture (87%) of the isomers 6 and A6 was obtained when the catalyst was potassium carbonate]. In a similar reaction *syn*-(methyl,carboethoxymethyl)bimane 7 (15%) with the *anti* isomer A7 (36%) was obtained from 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one 10c. *syn*-(Methyl,  $\beta$ -acetoxyethyl)bimane 8 (70%) was obtained from 3-methyl-4- $\beta$ -acetoxy-ethyl-4-chloro-2-pyrazolin-5-one 10d (potassium carbonate catalysis) and was converted by hydrolysis to *syn*-(methyl, $\beta$ -hydroxyethyl)bimane 9 (40%). Acetyl nitrate (nitric acid in acetic anhydride) converted *anti*-(amino,hydrogen)bimane 11 to *anti*-(amino,ni-tro)bimane 15 (91%), *anti*-(methyl,hydrogen)bimane 13 to *anti*-(methyl,nitro)(methyl,hydrogen)bimane 16 (57%), and degraded *syn*-(methyl,hydrogen)bimane 12 to an intract-able mixture. Treatment with trimethyl phosphite converted *syn*-(bromomethyl,methyl)-bimane 17 to *syn*-(dimethoxyphosphinylmethyl,methyl)bimane 18 (78%) that was further converted to *syn*-(styryl,methyl)bimane 19 (29%) in a condensation reaction with benzal-dehyde. Treatment with acryloyl chloride converted *syn*-(hydroxymethyl,methyl)bimane 20 to its acrylate ester 21 (22%). Stoichiometric bromination of *syn*-(methyl,methyl)-bimane 1 gave a monobromo derivative that was converted *in situ* by treatment with po-tassium acetate to *syn*-(acetoxymethyl,methyl)(methyl,methyl)bimane 47. N-Amino- $\mu$ -amino-*syn*-(methylene, methyl)bimane 24 (68%) was obtained from a reaction between the



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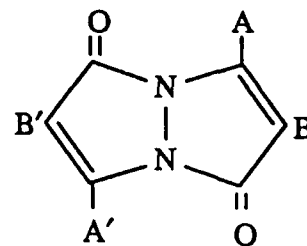
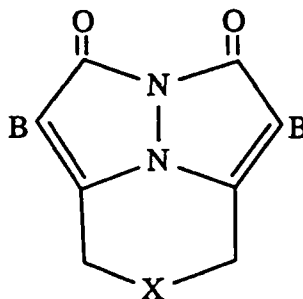
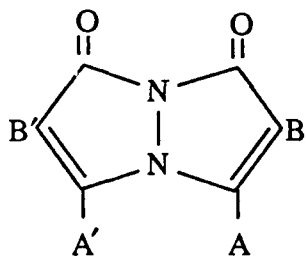
dibromide 17 and hydrazine. Derivatives of the hydrazine 24 included a perchlorate salt and a hydrazone 25 derived from acetone. Dehydrogenation of *syn*-(tetramethylene)bi-mane 26 by treatment with dichlorodicyanobenzoquinone (DDQ) gave *syn*-(benzo,tetra-methylene)bimane 27 (58%) and *syn*-(benzo)bimane 28 (29%). Bromination of the bimane 26 gave a dibromide 29 (92%) that was also converted by treatment with DDQ to *syn*-(benzo)bimane 28. Treatment with palladium (10%) on charcoal dehydrogenated 5,6,10,11-tetrahydro-7*H*,9*H*-benz[6,7]indazol[1,2-*a*]benz[*g*]indazol-7,9-dione 35 to *syn*-( $\alpha$ -naphtho)bimane 36 (71%). The bimane 35 was prepared from 1,2,3,4-tetrahydro-1-oxo-2-naphthoate 37 by stepwise treatment with hydrazine to give 1,2,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one 38, followed by chlorine to give 3*a*-chloro-2,3*a*,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one 39, and base. Dehydrogenation over palladium converted the indazolone 34 to 1*H*-benz[*g*]indazol-3-ol 36. Helicity for the hexacyclic *syn*-( $\alpha$ -naphtho)bimane 36 was confirmed by an analysis based on molecular modeling.

The relative efficiencies (RE) for laser activity in the spectral region 500–530 nm was obtained for 37 *syn*-bimanes by reference to coumarin 30 (RE 100): RE > 80 for *syn*-bimanes 3, 5, 18, and  $\mu$ -(dicarbomethoxy)methylene-*syn*-(methylene,methyl)bimane 50: RE 20-80: for *syn*-bimanes 1, 2, 4, 20, 24, 26, and  $\mu$ -thia-*syn*-(methylene,methyl)bimane 50: and RE 0-20 for 26 *syn*-bimanes. The bimane dyes tended to be more photostable and more water soluble than coumarin 30. The diphosphonate 18 in dioxane showed laser activity at 438 nm and in water at 514 nm. Presumably helicity, that was demonstrated by molecular modeling, brought about a low fluorescence intensity for *syn*-( $\alpha$ -naphtho)bimane 36,  $\Phi$  0.1, considerably lower than obtained for *syn*-(benzo)bimane 28,  $\Phi$  0.9.

Introduction. Following its discovery in 1966 the dye laser [1] depended on the availability of laser dyes to provide coherent light over the spectral region from ultraviolet to infrared. This laser activity was obtained from cyanine, xanthene (including rhodamine and fluorescein), triarylmethane, acridine, azine, and chlorophyll dyes; linear and condensed polycyclic benzenoid molecules; and certain heterocycles that included coumarins, quinolones, oxazoles, pyrazolines, and furans. In 1984 over 600 laser dyes were listed [2].

Parameters for a laser dye included high quantum fluorescence yield, (generally  $\Phi > 0.7$ ), minimal overlap of fluorescence with onset of absorption (S-S) and triplet-triplet (T-T) spectral regions, photostability, efficiency in power output, favorable solubility and interaction with the solvent, and availability [3]. Other factors also contributed to the laser performance. Aqueous solutions of a dye ( $10^{-4}$  molar was generally desirable) offered the superior thermo-optic properties of water that often improved laser activity [5c]. Groups that enhanced intersystem crossing ( $S_1 \rightarrow T_1$ ) through the heavy atom effect could interfere with laser activity and were generally avoided [3]. It was sometimes assumed that somewhat less than expected laser power output was the result of (1) nonradiative transfer ( $S_1 \rightarrow S_0$ ), (2) loss of electronic excitation through reversible charge transfer with the chromophore, and/or (3) self-quenching through dye aggregation [3]. About 125 tunable laser dyes more or less satisfied these special conditions and became commercially available to cover the region from 300 to 1200 nm [4].

Other investigations led us to examine *syn*-bimanes (1,5-diazabicyclo[3.3.0]octadien-2,8-diones) as laser dyes. Kosower introduced a system of trivial nomenclature for the bimanes based on substitution types. Type I: *syn*-(A,B)bimanes, Type II: *syn*-(A,B)(A',B')-bimanes, Type III:  $\mu$ -X-*syn*-(methylene,methyl)bimanes, Type IV: *anti*-(A,B)bimanes, and Type V: *anti*-(A,B)(A',B')bimanes were adopted for this report [6,7].



Type I: A,B = A',B'

Type II: A,B  $\neq$  A',B'

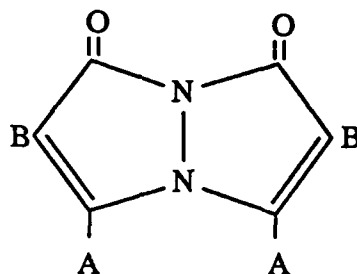
Type III: X = C,N,S

Type IV: A,B = A',B'

Type V: A,B  $\neq$  A',B'

Laser activity in the spectral region 500–530 nm from *syn*-(methyl,methyl)bimane 1 was reported in 1986 [5a]. The discovery of similar activity from *syn*-(methyl,chloro)-

bimane 2, *syn*-(acetoxymethyl,methyl)bimane 3, *syn*-(fluoromethyl,methyl)bimane 4, and  $\mu$ -(dicarboethoxy)methylene-*syn*-(methylene,methyl)bimane 5 followed rapidly [5b-d]. In our ongoing search for laser dyes it became desirable to examine greater diversification in substitution patterns in *syn*-bimanes.



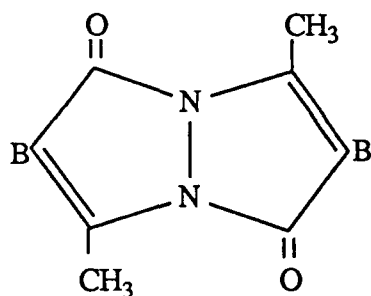
<u>Cpd</u>	<u>A</u>	<u>B</u>	<u>Cpd</u>	<u>A</u>	<u>B</u>
<u>1</u>	CH <sub>3</sub>	CH <sub>3</sub>	<u>12</u>	CH <sub>3</sub>	H
<u>2</u>	CH <sub>3</sub>	Cl	<u>17</u>	BrCH <sub>2</sub>	CH <sub>3</sub>
<u>3</u>	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	<u>18</u>	(CH <sub>3</sub> O) <sub>2</sub> P(O)CH <sub>2</sub>	CH <sub>3</sub>
<u>4</u>	FCH <sub>2</sub>	CH <sub>3</sub>	<u>19</u>	C <sub>6</sub> H <sub>5</sub> CH=CH	CH <sub>3</sub>
<u>6</u>	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<u>20</u>	HOCH <sub>2</sub>	CH <sub>3</sub>
<u>7</u>	CH <sub>3</sub>	CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	<u>21</u>	CH <sub>2</sub> =CHOCOCH <sub>2</sub>	CH <sub>3</sub>
<u>8</u>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> CCH <sub>3</sub>	<u>43</u>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
<u>9</u>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OH	<u>44</u>	C <sub>6</sub> H <sub>5</sub>	Cl
			<u>45</u>	C <sub>2</sub> H <sub>5</sub> OCO	Cl

### *syn*-Bimane Dye Preparations and Properties.

Background Information. Variation in substitution patterns in *syn*-bimanes has remained limited. In the Kosower scheme for their synthesis chlorination of a pyrazolinone followed by treatment with a base (potassium carbonate or a tertiary amine) brought about the formation of mixtures of *syn*- and *anti*-bimanes, eq (1) [6-8]. Selected conversions afforded preparative amounts of *syn*-bimanes with a limited range of substituents. *syn*-Bimanes with strong electron donating or withdrawing substituents were not prepared by

this method and remain largely unknown. The chemical reactivity needed for further conversion of a substituent, e.g., methyl to acetoxymethyl [8] was restricted to the short axis where substituents ran parallel with the NN bond.

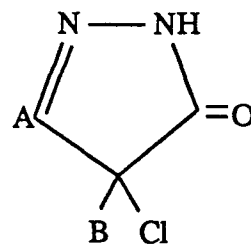
Chemical reactivity, "normal" positions of NMR signals, and the occurrence of planar and nonplanar molecules in the crystal were properties that supported the perception of *syn*- and *anti*-bimanes as examples of  $\alpha,\beta$ -unsaturated amide systems with no implication of "aromatic character"[6]. The fluorescence,  $\Phi > 0.7$ , from many *syn*-bimanes was, nevertheless, assumed to be a property of aromaticity insofar as strong fluorescence from an organic compound that was not aromatic has remained virtually unknown [5b]. A weak fluorescence from *anti*-bimanes [6] was shared with other pyrazolinones [9],  $\gamma$ -pyridones [10], maleimides [11], and presumably other quasiaromatic cyclic amides and hydrazides. A strong phosphorescence was noted for *anti*- but not for *syn*-bimanes [6].



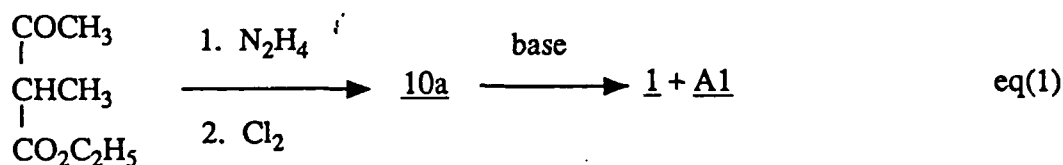
A1 B = CH<sub>3</sub>

A6 B = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>

A7 B = CH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>



<u>Cpd</u>	A	B
<u>10a</u>	CH <sub>3</sub>	CH <sub>3</sub>
<u>10b</u>	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>
<u>10c</u>	CH <sub>3</sub>	CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>
<u>10d</u>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> CCH <sub>3</sub>
<u>10e</u>	H	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>

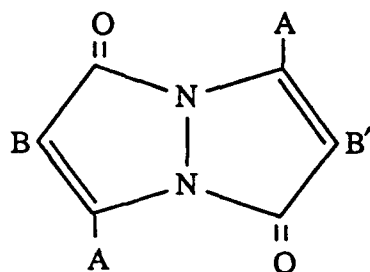




Long axis (perpendicular to the NN bond) substitution. *syn*-(Methyl,benzyl)bimane 6 was prepared from 3-methyl-4-benzyl-4-chloro-2-pyrazolin-5-one 10b (obtained from ethyl benzylacetoacetate by treatment with hydrazine followed by chlorination) under the influence of a novel catalyst [12] that was provided by a mixture of potassium fluoride and alumina. Formation of the *anti* isomer A6 was not detected; however, a mixture (1:1) of the isomers 6 and A6 was obtained when potassium carbonate was the catalyst. In related conversions 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one 10c (from diethyl acetosuccinate) gave *syn*-(methyl,carboethoxymethyl)bimane 7 along with the *anti* isomer A7, and 3-methyl-4- $\beta$ -acetoxyethyl-4-chloro-2-pyrazolin-5-one 10d (from ethyl  $\beta$ -acetoxyethylacetoacetate) gave *syn*-(methyl, $\beta$ -acetoxyethyl)bimane 8. Hydrolysis converted the latter to *syn*-(methyl, $\beta$ -hydroxyethyl)bimane 9. Attempts to obtain *syn*-(hydrogen,carboethoxy)bimane from ethoxymethylenemalonic ester were unsuccessful. Treatment with hydrazine converted the ester to a pyrazolinone that underwent chlorination to a product thought to be the chloropyrazolinone 10e; however, the latter in the presence of base resisted conversion to a bimane.

To enhance bimane functionality an exploratory investigation of the aromatic nitration of *anti*-(amino,hydrogen)bimane 11 (the *syn* isomer is unknown) and *syn*- and *anti*-(methyl,hydrogen)bimanes 12 and 13 was undertaken. The *anti*-bimane 11 was obtained from N,N'-dicyanoacetohydrazide 14 [(NHCOCH<sub>2</sub>CN)<sub>2</sub>] by cyclization in the presence of sodium bicarbonate [13]. Acetyl nitrate (explosive above 50 °C), prepared *in situ* from a mixture of nitric acid (90%) and acetic anhydride, converted the *anti*-bimane 11 to *anti*-(amino, nitro)bimane 15, a structure assignment supported by IR, <sup>13</sup>C NMR, EI-MS, and elemental analysis. Similar treatment converted *anti*-(methyl,hydrogen)bimane 13 [5] to *anti*-(methyl, nitro)(methyl,hydrogen)bimane 16. *syn*-(Methyl,hydrogen)bimane 12 [5] was completely converted by similar treatment to an intractable mixture that contained no more than a trace amount of a solid thought to be a mononitro derivative on the basis of M<sup>+</sup> 209 in the EI-MS. These aromatic substitution reactions resembled nitrations of pyrazolinones, hydroxy-, and aminopyrazoles [14] and tended to support quasiaromaticity of

the bimanane ring systems (see above).



11 A = NH<sub>2</sub>, B = B' = H

13 A = CH<sub>3</sub>, B = B' = H

15 A = NH<sub>2</sub>, B = B' = NO<sub>2</sub>

16 A = CH<sub>3</sub>, B = NO<sub>2</sub>, B' = H

Attempts to oxidize amino groups in bimananes 11 and 15 to nitro groups were unsuccessful and led instead to intractable mixtures. An unidentified product isolated as a hydrated dipotassium salt C<sub>6</sub>N<sub>4</sub>O<sub>8</sub>K<sub>2</sub> · 1.5 H<sub>2</sub>O from a treatment of diaminodinitrobimane 15 with potassium superoxide represented the oxidation level of a dihydroxydinitrobimane, in which hydroxyl groups had replaced amino groups. A hydrated sodium salt of a dihydroxydinitrobimane C<sub>6</sub>H<sub>4</sub>O<sub>8</sub>Na<sub>2</sub> · 1.5 H<sub>2</sub>O, was previously obtained in an oxidation of the corresponding dioxime [15].

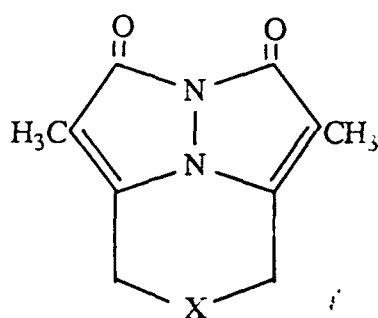
The accessibility of substituted *syn*-bimananes was restricted by degradation of the bimane structure when treated under mild conditions with either an oxidizing reagent or an acid and, as previously reported [6], by ring conversion under alkaline conditions.

Short axis (parallel to the NN bond) substitution. Generally substituent variation proceeded from the non-fluorescent *syn*-(bromomethyl,methyl)bimane 17 [obtained from *syn*-(methyl,methyl)bimane 1 by bromination] [7]. Conversion of the dibromide 17 to *syn*-(dimethoxyphosphinylmethyl, methyl)bimane 18 was brought about by treatment with trimethylphosphite. A need for polymerizable *syn*-bimane monomers to be formulated into glassy polymer slugs led to the preparation of *syn*-(styryl,methyl)bimane 19 (from the diphosphonate 18 and benzaldehyde) and the acrylate ester 21 of *syn*-(hydroxymethyl, methyl)bimane 20 (from the dibromide 17 by treatment with alkali followed by esterification of the glycol 20 with acryloyl chloride). Laser activity from dyes in polymeric glasses [16] will be described elsewhere.

Stoichiometry controlled a monobromination of the bimanane 1 [6,8]. Without isolation the bromide was treated with potassium acetate to give *syn*-(acetoxymethyl,methyl) (methyl,methyl)bimane 47.

$\mu$ -Bridged *syn*-bimanes. Ring closure between short axis methyl substituents by a one atom bridge afforded  $\mu$ -bridged *syn*-bimanes [7]. These tricyclic heterocycles were generally obtained from the dibromide 17 in reactions with nucleophiles. We repeated Kosower's preparation of  $\mu$ -(dicarboethoxy)methylene-*syn*-(methylene, methyl)bimane 5 from the dibromide 17 in a reaction with malonic ester [7], and similarly prepared the homologous dimethyl ester 22. The diester 5 was converted by hydrolysis with decarboxylation to the monocarboxylic acid 23 [7]. Our attempts to convert the acid to its sodium salt were unsuccessful; mild treatment with sodium hydroxide, sodium bicarbonate, sodium alkoxide, or sodium hydride gave intractable mixtures, in agreement with a known instability of the bimanane nucleus toward alkali [6].

By replacing ammonia with hydrazine in Kosower's scheme for converting *syn*-(bromomethyl,methyl)bimane 17 to  $\mu$ -amino-*syn*-(methylene,methyl)bimane 53 [7] the corresponding N-amino derivative 24 was obtained without competitive formation of the cyclic hydrazine isomer (with an eight-membered ring). The hydrazine 24 was characterized by conversion to its perchlorate salt and to the hydrazone derivative 25 obtained from acetone.



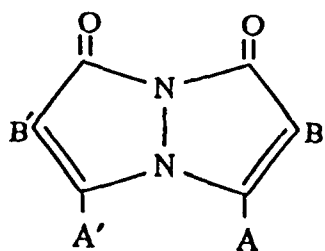
<u>Cpd</u>	<u>X</u>	<u>Cpd</u>	<u>X</u>
<u>5</u>	C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<u>50</u>	S
<u>22</u>	C(CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	<u>51</u>	SO <sub>2</sub>
<u>23</u>	CHCO <sub>2</sub> H	<u>52</u>	C(CN) <sub>2</sub>
<u>24</u>	NNH <sub>2</sub>	<u>53</u>	NH
<u>25</u>	NN=C(CH <sub>3</sub> ) <sub>2</sub>	<u>54</u>	NCOCH <sub>3</sub>
<u>49</u>	NCH <sub>2</sub> CH <sub>2</sub> OH	<u>55</u>	NCOCF <sub>3</sub>

*syn*-(Benzo)- and *syn*-( $\alpha$ -naphtho)bimanes **28** and **36**. Dehydrogenation of the previously reported *syn*-(tetramethylene)bimane (**26**) [6] by treatment with dichlorodicyanobenzoquinone (DDQ) afforded both *syn*-(benzo)bimane **28** and the intermediate *syn*-(benzo,tetramethylene)bimane **27**. Attempted dehydrogenation of bimane **26** by treatment with either 1,4-chloranil or palladium (10%) on charcoal was unsuccessful.

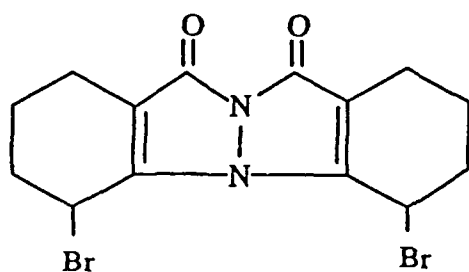
Bromination converted the bimane **26** to a dibromide that was given the tentative assignment of 4,6-dibromo-1,2,3,4,6,7,8,9-octahydro-10*H*,12*H*-indazolo[1,2-*a*]indazol-10,12-dione **29**. Treatment with an excess of DDQ converted the dibromide **29** to *syn*-(benzo)bimane **28**. The formation of a bromo derivative of bimane **28** was not detected.

An alternative approach to the preparation of *syn*-(benzo)bimane **28** that called for dehydration with cyclization of *N,N*-di-*o*-carboxyphenylhydrazine **32** was abandoned when the corresponding nitrosamine precursor **31** was not obtained by the treatment of di-*o*-carboxyphenylamine **30** [17] with nitrosating agents. A related conversion of *N,N'*-di-*o*-carboxyphenylhydrazine **33** [(*o*-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>] to *anti*-(benzo)bimane **34** was reported in 1916 [18].

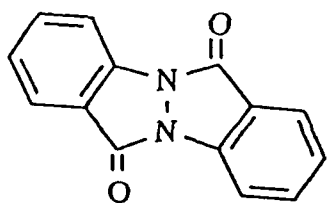
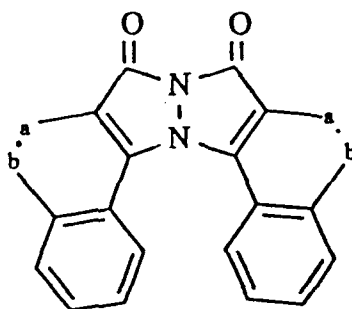
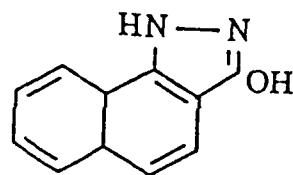
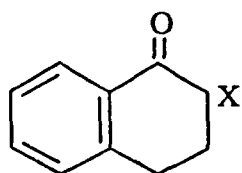
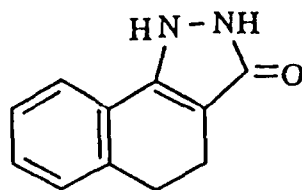
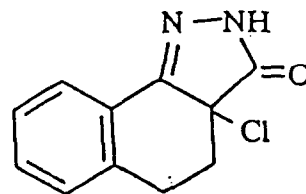
*syn*-( $\alpha$ -Naphtho)bimane **36** was similarly obtained by a dehydrogenation of 5,6,10,11-tetrahydro-7*H*,9*H*-benz[6,7]indazolo[1,2-*a*]benz[*g*]indazol-7,9-dione **35** by treatment with palladium (10%) on charcoal. The bimane **35** was prepared from ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate **37** [19] by treatment with hydrazine to give 1,2,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one **38** followed by chlorination to give 3*a*-chloro-2,3*a*,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one **39** and treatment with potassium carbonate. A structure confirmation of the indazolone **38** was provided by its dehydrogenation over palladium to give 1*H*-benz[*g*]indazol-3-ol **40**. In the absence of an X-ray crystallographic analysis, precluded by inability to obtain a crystalline modification, helicity for bimane **36** was confirmed by an analysis based on molecular modeling. In contrast to the *syn*-(benzo)bimane **28** in which the carbon atoms attached to the axial substitution sites are calculated to lie in the molecular plane, the corresponding carbon atoms in the *syn*-( $\alpha$ -naphtho)bimane **36** are calculated to be displaced by 0.53Å above and below the mean molecular plane.



<u>Cpd.</u>	<u>A,B</u>	<u>A',B'</u>
<u>26</u>	$(\text{CH}_2)_4$	$(\text{CH}_2)_4$
<u>27</u>	$(\text{CH}_2)_4$	$(\text{CH})_4$
<u>28</u>	$(\text{CH})_4$	$(\text{CH})_4$
<u>46</u>	$\text{HOCH}_2, \text{CH}_3$	$\text{CH}_3, \text{CH}_3$
<u>47</u>	$\text{CH}_3\text{CO}_2\text{CH}_2, \text{CH}_3$	$\text{CH}_3, \text{CH}_3$

29 $(o\text{-HO}_2\text{CC}_6\text{H}_4)_2\text{NX}$ 

<u>30</u>	$\text{X} = \text{H}$
<u>31</u>	$\text{X} = \text{NO}$
<u>32</u>	$\text{X} = \text{NH}_2$

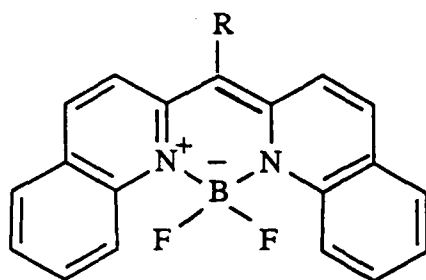
3435  $a \cdot b = \text{CH}_2\text{CH}_2$ 36  $a \cdot b = \text{CH}=\text{CH}$ 4037  $\text{X} = \text{CO}_2\text{C}_2\text{H}_5$ 3839

### syn-Bimane Laser Activity.

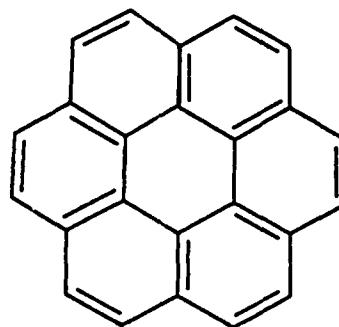
Background information. In water *syn*-(methyl,hydrogen)bimane 12 [6] showed fluorescence  $\lambda_{\text{max}}$  430 nm ( $\Phi = 0.7$ ), T-T absorption  $\lambda_{\text{max}}$  490 nm with a shoulder at  $\lambda$  420 nm, and no laser activity [20]. For comparison *syn*-(methyl,methyl)bimane 1 in water showed fluorescence  $\lambda_{\text{max}}$  480 nm ( $\Phi = 0.7$ ), the same T-T absorption curve, and broadband laser activity at  $\lambda$  504 nm [5a]. It was suggested that a long axis methyl substituent introduced a red shift solvatochromic effect on the fluorescence of the bimane 1 in water that promoted its laser activity above 500 nm where T-T absorption had steeply declined in intensity [5a]. The lasing efficiency (about 40 percent as efficient as coumarin 30) [21] was low – presumably a consequence of declining fluorescence intensity in the same spectral region [5a]. An absence of detectable laser activity from the bimane 1 in ethanol or in *p*-dioxane was attributed to solvatochromic shifts in fluorescence  $\lambda_{\text{max}}$  to 460 and 420 nm respectively where T-T absorption was more intense [5a]. Laser activity for *syn*-(hydrogen,methyl)-bimane Type I (A = H, B = CH<sub>3</sub>), fluorescence  $\lambda_{\text{max}}$  460 nm ( $\Phi = 0.6$ ) [22], was not investigated; therefore a short axis methyl substituent effect on laser activity was not directly established.

A study of the polarization of low energy electronic transitions (S-S and T-T) revealed the presence of two differently polarized T-T transitions in the spectral region of fluorescence for *syn*-bimanes. This increased the complexity of both long and short axis substituent effects on the T-T absorption and indirectly on the laser activity for *syn*-bimanes [20]. Investigations are planned to unravel these and other polarization effects in bimanies.

Angular *endo*-annulation was found in the laser active "boradiazinium salt" 41 [23] but was not extended to test the possibility of a helical laser dye. That helicity could create an interference with luminescence was shown in an examination of a series of hydrocarbons in which progressive helicity correlated with diminished fluorescent intensity [24]. Presumably laser activity in coronene 42 [25] was enhanced by chromophore planarity. We report the angular *endo*-annulation of *syn*-bimane into 4-ring and 6-ring systems.



41 R = 2-isoquinolyl



42

**Results and Discussion.** *syn*-Bimane derivatives offered a promising new source of laser dyes for the spectral region 500-530 nm. An examination of 18 Type I, two Type II, 13 Type III, and four annelated *syn*-bimanes revealed significant laser activity in eight from Types I and II (Table 1) and five from Type III (Table 2). Relative efficiencies, RE ( $\pm 10\%$ ), in laser power output were determined by comparison with the performance shown by a  $7.5 \times 10^{-4}$  molar solution in ethanol of coumarin 30 (RE arbitrarily 100). Bimanes 3, 5, 18, and 22 (Tables 1 and 2) gave RE  $> 80$ . Each of these four dyes offered a high quantum fluorescence yield ( $\Phi > 0.7$ ), solvatochromic control of interference from absorption (S-S and T-T), superior photostability, and availability. In addition dyes 3 and 18 were water soluble.

Table 1.

Table 2.

A replacement of the ester groups in dye 5 (or 22) with cyano groups offered the strongly fluorescent  $\mu$ -dicyanomethylene-*syn*-(methylene,methyl)bimane 52 (RE 0). A complete inhibition of laser activity in 52 was attributed in part to an electronic interaction between the cyano groups and the nearby chromophore. (In other examples inhibition of luminescence was attributed to a similar interaction between nitro and chromophore groups. [3]). The conspicuous absence of a cyano derivative in current lists of dyes [2-4] was taken as an indication that the cyano group within the dye molecule generally quenched laser activity.

The diphosphonate 18 was noted for a solvatochromic effect that shifted its fluorescence maximum from 425 nm in dioxane to 460 nm in water without shifting T-T absorption at about 480 nm to afford laser activity at 438 nm in one and at 514 nm in the other solvent (Fig 1,2). In water the solubility of the diphosphonate 18 (0.2 M) surpassed coumarin 30 (less than  $10^{-4}$  M) but was 20 percent less power efficient (Fig 3) when each was pumped to 4.5 J. The diphosphonate 18 showed good photostability; however, after exposure in methanol to irradiation at 250 nm for one week it was completely converted to unidentified material. Under similar prolonged irradiation *syn*-(methyl,methyl)bimane 1, a red solid, was converted to an unknown colorless powder.

Figure 1.

Figure 2.

Figure 3.

Dyes that showed RE 20-80 included the bimanes 1 [5a], 2 [5b], 4 [5b], 20, and 26 (Table 1); and bimanes 24 and 50 (Table 2). A long axis alkyl substituent effect that was discovered for the methyl group in bimane 1 [5a] was greatly diminished in *syn*-(tetramethylene)bimane 26 and was ineffective in bimanes 6-9 that were laser inactive. The performance (RE 42) that was characteristic of *syn*-(methyl,chloro)bimane 2,  $\Phi$  0.8, (Table 1) was not shared with *syn*-(carboethoxy,chloro)bimane 45,  $\Phi$  0.1, (inactive) and *syn*-(phenyl,chloro)bimane 44,  $\Phi$  0.6, (inactive). Although these results are in line with the general requirement for the presence of strong fluorescence, the laser inactivity in the latter example was attributed in part to interference from an assumed T-T absorption (phenyl group).

The results obtained from *syn*-(hydroxymethyl,methyl)bimane 20,  $\Phi$  0.60, (RE 67) and *syn*-(hydroxymethyl,methyl)(methyl,methyl)bimane 46,  $\Phi$  0.80, (RE 19) (Table 1) appeared to be in conflict; however, a decrease in the laser activity of the alcohol 46 was attributed to its rapid photodecomposition, a property not shared with the other bimanes in this report. Although a lower performance rating for the glycol 20 (RE 67), relative to its diacetate ester 3 (RE 89), could be attributed to self-quenching brought about by dye aggregation as a



result of hydrogen bonding, a parallel improvement in the performance of the alcohol 46 (RE 19) on conversion to its acetate ester 47 (RE < 19) was not observed.

Our results indicated that biman laser dyes with  $\mu$ -heteroatom bridges did not afford superior performances. No laser activity was detected from  $\mu$ -amino-*syn*-(methylene, methyl)bimane 53, its N- $\beta$ -hydroxyethyl derivative 49, and its N-acetyl derivative 54. Weak performances were found in the N-trifluoroacetyl derivative 55 (RE 13) and the N-amino derivative 24 (RE 51) (Table 2). There was some improvement shown by  $\mu$ -thia-*syn*-(methylene, methyl)bimane 50 (RE 61); however,  $\mu$ -sulfonyl-*syn*-(methylene, methyl)-bimane 51 was laser inactive. Laser inhibition as a result of an electronic interaction between amino, thia, or sulfonyl bridges and the nearby chromophore was assumed.

Strong T-T absorption for *syn*-(benzo)bimane 28 was shown to interfere throughout the fluorescence spectral region [20] and presumably quenched laser activity. A similar quenching effect was assumed for the related bimanenes 27 and 35. The absence of laser activity in bimanenes 17, 29, 44, and 45 was partially attributed to the heavy atom effect. A low fluorescence quantum yield,  $\Phi$  0.1, for laser inactive *syn*-( $\alpha$ -naphtho)bimane 36 (compare  $\Phi$  0.9 for *syn*-(benzo)bimane 28) was attributed to further disruption in the planarity of the bimane chromophore that was presumably brought about by helicity.

### Experimental.

Spectral data was obtained from the following instruments: Pye-Unicam SP 200 IR, Varian A-60 and JEOL FX Q NMR, Hewlett-Packard 5985 (70 eV) (GC-MS), Beckman DU (UV), and a Perkin-Elmer LS-5B Luminescence Spectrometer. A dye laser was constructed at the Naval Ocean Systems Center [26]. It operated in the nonflowing (static) mode and had no tuning capability. The dye cell (2.5 mm diam., 50 mm long) had an elliptical cavity configuration of small eccentricity. The flashlamp pulser, EG & G model FX 139C-2, had a rise time of 200 ns, half-width length of 600 ns, and input energy of 2 J at 6.32 kV, 5 J at 10.00 kV, 7.2 J at 12.00 kV, and 10 J at 14.14 kV [5a]. Laser energy outputs were measured with an accuracy of  $\pm$  5% by a Scientech 365 power and energy

meter [5c]. Laser activities are described in Tables 1 and 2.

For each product the IR spectrum agreed with the literature data and/or supported the assigned structure. Each recorded UV absorption was restricted to the highest wave length. H NMR (60 MHz) spectra were run in  $\text{CDCl}_3$  with tetramethylsilane as an internal standard.  $^{13}\text{C}$  NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference. The central peak of the solvent multiplet signal was assigned:  $\delta$  77.00 ( $\text{CDCl}_3$ ), 39.50 ( $(\text{CD}_3)_2(\text{SO})$ ). Fluorescence quantum yields were determined by reference to *syn*-(methyl, methyl)bimane 1,  $\Phi$  0.72 [6], *syn*-(benzo)bimane 28,  $\Phi$  0.9 [27], and/or quinine sulfate,  $\Phi$  0.55. The latter reference was abandoned for several determinations when it led to erratic results. The mass spectra were electron impact (70 eV). Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, Indiana and Galbraith Laboratories, Inc., Knoxville, Tenn. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). Triplet extinction coefficients over the laser action spectral region of the dye were measured at the temperature of liquid nitrogen by equipment previously described [28] using McClure's method [29]. Molecular mechanics calculations were performed on a MicroVAX 2000 computer with Evans and Sutherland PS390 graphics display using the BIOGRAF [30] software package. The force field parameters were taken from the MM2 set [31].

Solvents, reagents, and starting materials that were obtained from the Aldrich Chemical Company, Milwaukee, WI included acetic anhydride, acetone, acetonitrile, acryloyl chloride, alumina, ammonium chloride, benzaldehyde, benzene, bromine,  $\beta$ -bromoethyl acetate, carbon tetrachloride, celite, *m*-chloroperbenzoic acid, chloroform- $d$ , dichlorodicyano-benzoquinone (DDQ), dichloromethane, diethyl acetylsuccinate, diethyl carbonate, diethyl ethoxymethylenemalonate, *N,N*-disopropylethylamine, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide- $d_6$  ( $\text{DMSO}-d_6$ ), *p*-dioxane, 18-crown-6-ether, ethanol, ethyl acetate, ethyl benzylacetoacetate, hexane, hexafluoroisopropanol, hydrazine hydrate, iodobenzene

diacetate, isopropanol, methanol,  $\alpha$ -methyltetrahydrofuran, nitric acid, palladium (10% on charcoal), perchloric acid, peroxytrifluoroacetic acid, petroleum ether, potassium bromide, potassium *tert*-butoxide, potassium carbonate, potassium fluoride, potassium superoxide, silica gel (230–400 mesh, 60 Å), sodium bicarbonate, sodium hydride, sodium hydroxide, sodium sulfate, tetrahydrofuran (THF),  $\alpha$ -tetralone, *p*-toluenesulfonic acid, triethylamine, trifluoroacetic anhydride, trifluoroethanol, and trimethyl phosphite. Coumarins 6, 30, 120, and 314, rhodamine 6G, sulforhodamine B and thin layer chromatography sheets were obtained from Eastman Kodak Co., Rochester, NY. Chlorine was obtained from Matheson Gas Products, Secaucus, NJ. Nitrogen was obtained from Air Products and Chemicals, Inc., Allentown, PA. Hydrogen peroxide (90%) was obtained from Shell Chemical Company, Houston, Texas.

The following compounds were prepared according to the directions cited: bimanies type I: *syn*-(A,B)bimanies where (A,B) was (methyl,hydrogen) in 12 [6], (methyl,methyl) in 1 [6], (bromomethyl,methyl) in 17 [6,8], (hydroxymethyl,methyl) in 20 [8], (tetramethylene) in 26 [6], (methyl,phenyl) in 43 [6], (phenyl,chloro) in 44 [6], and (carboethoxy,-chloro) in 45 [22]; bimanies type II: *syn*-(hydroxymethyl,methyl)(methyl,methyl)bimane 46 [6]; bimanies type III:  $\mu$ -X- *syn*-(methylene,methyl)bimanies where X was dicarboethoxymethylene in 5 [7], dicarbomethoxymethylene in 22 [7], carboxymethylene in 23 [7], thia in 50 [7], sulfono in 51 [7], dicyanomethylene in 52 [7], amino in 53 [7], and acetylamino in 54 [7]; bimanies type IV: *anti*-(methyl, hydrogen)bimane 13 [6] and *anti*-(amino,hydrogen)bimane 11 [13]; miscellaneous: 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one 10c [32], 4- $\beta$ -acetoxyethylethyl-3-methyl-2-pyrazolin-5-one [33], and ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate 37 [19].

3-Methyl-4-benzyl-4-chloropyrazol-2-in-5-one 6b. Hydrazine hydrate (10.5 g, 0.21 mol) in methanol (20 mL) was added slowly with stirring to ethyl benzylacetoacetate (44.0 g, 0.2 mol) in methanol (200 mL). The mixture was heated at 65 °C for one h and cooled to bring about the precipitation of 3-methyl-4-benzyl-2-pyrazolin-3-one that recrystallized from ethanol as a colorless solid, 32.0 g (85%), mp 230–231 °C (lit. [34] 232 °C); H NMR

(CDCl<sub>3</sub>):  $\delta$  2.0 (s, 3 H, CH<sub>3</sub>), 3.6 (s, 2 H, CH<sub>2</sub>), and 7.2 (s, 5 H, C<sub>6</sub>H<sub>5</sub>). A solution of the pyrazolinone (32.0 g, 0.17 mol) in dichloromethane (300 mL) was treated with a stream of chlorine gas until the solid phase disappeared and the solution became yellow. Traces of chlorine were removed by purging with a stream of nitrogen. The solvent was removed to leave a yellow oil that recrystallized from benzene to give the chloropyrazolinone 10b as a yellow solid, 32.5 g (86%); mp 75–76 °C; H NMR (CDCl<sub>3</sub>):  $\delta$  2.1 (s, 3 H, CH<sub>3</sub>), 3.3 (d, 2 H, CH<sub>2</sub>), 7.2 (s, 5 H, C<sub>6</sub>H<sub>5</sub>), 8.9 (broad, 1 H, NH). Anal. calcd for C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>OCl: C, 59.32; H, 4.94; N, 12.58; Cl, 15.95. Found: C, 59.26; H, 5.08; N, 12.79; Cl, 15.90.

syn-(Methyl,benzyl)bimane 6. The prepared mixture (10 g) of potassium fluoride and neutral alumina (2:3 by wt) was added to the chloropyrazolinone 10b (1.0 g, 5 mmol) in dichloromethane (100 mL) at 10 °C and the mixture was stirred for one h. Filtration and concentration of the mother liquor left a residue that recrystallized from carbon tetrachloride to give the bimane 6 as a yellow crystalline solid, 0.5 g (62%); mp 124–125 °C; H NMR (CDCl<sub>3</sub>):  $\delta$  2.25 (s, 6 H, CH<sub>3</sub>), 3.6 (s, 4 H, CH<sub>2</sub>), 7.25 (s, 10 H, C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  159.78 (CO); 145.99 (O=CC=C); 138.58, 128.43, 128.04, and 126.22 (C<sub>6</sub>H<sub>5</sub>); 115.56 (O=C=C); 27.51 (CH<sub>2</sub>); 11.71 (CH<sub>3</sub>). UV (CH<sub>3</sub>CN):  $\lambda$  ( $\epsilon$ ) 375 (7916); fluorescence (dioxane):  $\lambda$  ( $\Phi$ ) 417 (0.8); EI-MS: 344 (M<sup>+</sup>). Anal. calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.74; H, 5.81; N, 8.13. Found: C, 76.52; H, 5.80; N, 8.25.

When the reaction was catalyzed by potassium carbonate a mixture (1:1) (87%) of the bimane 6 and its *anti* isomer A6 was obtained.

syn-(Methyl,carboethoxymethyl)bimane 7. To 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one (4.4 g, 20 mmol) in dichloromethane (200 mL) a prepared mixture (44 g) of potassium fluoride and neutral alumina (2:3 by wt) was added at 25 °C with stirring that was continued for one h. After filtration the mother liquor was concentrated to leave a brown solid that was purified by flash chromatography from a column of silica gel (dichloromethane) to give *anti*-(methyl,carboethoxymethyl)bimane A7 as a colorless solid, 1.2 g (36%), mp 183–184 °C (lit. [32] mp 180 °C), followed by the *syn* isomer 7 as a pale yellow solid, 0.5 g (15%); mp 146–147 °C; H NMR (CDCl<sub>3</sub>):  $\delta$  1.27 (t, 6 H, CH<sub>3</sub>), 2.4 (s,

6 H, CH<sub>3</sub>), 3.3 (s, 4 H, CH<sub>2</sub>), 4.13 (q, 4 H, CH<sub>2</sub>); UV (CH<sub>3</sub>CN):  $\lambda$  ( $\epsilon$ ) 370 (7303); fluorescence (ethanol):  $\lambda$  ( $\Phi$ ) 420 (0.8); EI-MS: 336 (M<sup>+</sup>). Anal. calcd for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>: C, 57.14; H, 5.92; N, 8.33. Found: C, 56.91; H, 5.71; N, 8.58. When an attempt to repeat the preparation with potassium carbonate as the catalyst was made the starting material was partially converted to a mixture of bimanes 3 and A3 after 20 h at 25 °C.

4-Acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one 10d. Chlorine gas was bubbled into a suspension of 4- $\beta$ -acetoxyethyl-3-methyl-2-pyrazolin-5-one (15.0 g, 80 mmol) in dichloromethane (500 mL) until the suspension dissolved to give a yellow solution. The solution was stirred for an additional thirty minutes. Excess chlorine and the solvent were removed under reduced pressure to give a yellow residue, which was recrystallized from a mixture of hexane and carbon tetrachloride to give 4-acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one 10d as a colorless crystalline solid, 13.5 g (76%); mp 94-95 °C; H NMR (CDCl<sub>3</sub>):  $\delta$  2.00 (s, 3 H, CH<sub>3</sub>), 2.14 (s, 3 H, CH<sub>3</sub>), 2.47 (t, 2 H, CH<sub>2</sub>), 4.05 (t, 2 H, CH<sub>2</sub>), 9.35 (br, 1 H, NH). Anal. calcd for C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>O<sub>3</sub>Cl: C, 43.95; H, 5.07; N, 12.81; Cl, 16.22. Found: C, 43.83; H, 5.04; N, 12.89; Cl, 16.66.

syn-(Methyl,acetoxyethyl)bimane 8. 4-Acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one 10d (5.0 g, 23 mmol), potassium carbonate (10.0 g, 72 mmol) and water (2 mL) were added to dichloromethane (300 mL). The resulting suspension was stirred vigorously for four hours. The reaction was monitored with thin-layer chromatography (ethyl acetate). Celite 545 (10 g) was then added, and the resulting mixture was passed through a short silica gel column (dichloromethane, 100 mL). The solvent was removed to give a yellow residue which was recrystallized from ethyl acetate to give 2.7 g (70%) of the bimane 8, mp 134-135 °C; H NMR (CDCl<sub>3</sub>):  $\delta$  2.03 (s, 3 H, CH<sub>3</sub>), 2.37 (s, 3 H, CH<sub>3</sub>), 2.62 (t, 2 H, CH<sub>2</sub>), 4.15 (t, 2 H, CH<sub>2</sub>); UV (H<sub>2</sub>O):  $\lambda$  ( $\epsilon$ ) 384 (6048); fluorescence (dioxane):  $\lambda$  ( $\Phi$ ) 457 (0.8). Anal. calcd for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.08; H, 6.57; N, 10.99.

syn-(Methyl,2-hydroxyethyl)bimane 9. syn-(Methyl,acetoxyethyl)bimane 8 (1.0 g, 3 mmol) and toluenesulfonic acid (20 mg) was dissolved in methanol (50 mL). The solution

was heated at 60 °C for 2 days, and the reaction was monitored with thin-layer chromatography (ethyl acetate). The solvent was removed to give a yellow residue which recrystallized in acetonitrile and dimethylformamide to give 0.30 g (40%) of the bimanane 9 mp 186.5–188 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>-DMSO-*d*<sub>6</sub>): δ 2.33 (t, 2 H, CH<sub>2</sub>) 2.39 (s, 3 H, CH<sub>3</sub>), 3.39 (t, 2 H, CH<sub>2</sub>), 3.77 (br, 1 H, OH); UV (H<sub>2</sub>O): λ (ε) 317 (23,048); fluorescence (dioxane): λ (Φ) 464 (0.5). Anal. calcd for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.08; H, 6.57; N, 10.99.

Ethyl 2-pyrazolin-5-one-4-chloro-4-carboxylate 10e. Hydrazine hydrate (5.5 g, 0.1 mol) in ethanol (20 mL) was added with stirring to a solution of diethyl ethoxymethylene malonate (21.6 g, 0.1 mol) in ethanol (200 mL). The mixture was heated at 80 °C for 18 h and cooled. Ethyl 2-pyrazolin-5-one-4-carboxylate precipitated and recrystallized from ethanol as a colorless crystalline solid, 7.5 g (48%); mp 177–178 °C (dec); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 1.2 (t, 3 H, CH<sub>3</sub>), 4.2 (q, 2 H, CH<sub>2</sub>), 7.9 (s, 1 H, CH); EI-MS: 156 (M<sup>+</sup>). Anal. calcd for C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>: C, 46.15; H, 5.12; N, 17.94. Found: C, 46.25; H, 5.13; N, 17.93. The pyrazolinone (5.0 g, 32 mmol) in dichloromethane (200 mL) was treated with a stream of chlorine gas at 25 °C until the solid phase disappeared and the solution became yellow. Excess chlorine was purged with a stream of nitrogen. Removal of the solvent left the chloropyrazolinone 10e or an isomer that recrystallized from benzene as a yellow solid, 5.5 g (90%); mp 103–105 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.3 (t, 3 H, CH<sub>3</sub>), 4.4 (q, 2 H, CH<sub>2</sub>), 7.4 (s, 1 H, CH), and 9.6 (broad, 1 H, CH). Anal. calcd for C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sub>3</sub>Cl: C, 37.79; H, 3.79; N, 14.69; Cl, 18.68. Found: C, 37.87; H, 3.57; N, 14.63; Cl, 18.72. Attempts to convert the product 10e (or isomer) under the catalysis of either potassium carbonate, or *N,N*-diisopropylethylamine, or potassium fluoride on alumina, or sodium hydride in tetrahydrofuran to ethyl *syn*-(hydrogen,carboxy)bimane were unsuccessful.

*anti*-(Methyl,nitro)(methyl,hydrogen)bimane 16. After a mixture of nitric acid (90%, 0.20 mL) and acetic anhydride (0.75 mL) was stirred at 0 °C for 15 m, *anti*-(methyl,hydrogen)bimane 13 (0.16 g, 1.0 mol) was added slowly. The mixture was stirred at 0 °C for 30 m and poured onto crushed ice to precipitate the nitrobimane 16 as an orange solid, 0.12 g

(57%), mp 196 °C (dec) (acetone). H NMR (CDCl<sub>3</sub>):  $\delta$  2.6 (s, 3 H, CH<sub>3</sub>), 3.0 (s, 3 H, CH<sub>3</sub>), and 5.5 (s, 1 H, CH); EI-MS: 209 (M<sup>+</sup>). Anal. calcd for C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O<sub>4</sub>: C, 45.94; H, 3.37; N, 20.09. Found: C, 45.62; H, 3.19; N, 19.59.

Attempts to extend the nitration reaction to *syn*-(methyl,hydrogen)bimane 12 gave intractable mixtures. A trace amount of solid was thought to be a *syn*-isomer of bimane 16 since the mass spectrometric analysis showed EI-MS 209 (M<sup>+</sup>).

*anti*-(amino,nitro)bimane 15. Following the above procedure *anti*-(amino,hydrogen)bimane 11 (0.4 g, 2.4 mol) in a mixture of nitric acid (90%, 0.7 mL) and acetic anhydride (2.0 mL) at 0 °C with stirring for 30 m gave the dinitrobimane 15 as a red orange solid, 0.56 g (91%), mp 318 °C (dec) (acetone). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  107.8, 151.3, and 153.7; EI-MS 256 (M<sup>+</sup>). Anal. calcd for C<sub>6</sub>N<sub>4</sub>N<sub>6</sub>O<sub>6</sub>: C, 28.13; H, 1.56; N, 32.81. Found: C, 28.07; H, 1.57; N, 32.07.

Oxidation of aminobimanes. The diaminobimane 11 in a mixture of trifluoroacetic anhydride and hydrogen peroxide (90%) was converted to an intractable yellow gum. The diaminodinitrobimane 15 was unaffected by *m*-chloroperbenzoic acid, or peroxytrifluoroacetic acid, or iodobenzene diacetate.

A slurry of the diaminodinitrobimane 15 (0.8 g, 3.1 mmol), 18-crown-6 ether (0.15 g), and potassium superoxide (1.0 gm 14.1 mmol) in benzene was stirred for 17 h at 25 °C under nitrogen. Addition of water gave a clear yellow aqueous layer that was acidified (dilute hydrochloric acid) to precipitate a trace amount of solid, mp > 300 °C, that was discarded. Addition of ethanol to the filtrate caused the precipitation of a potassium salt as a colorless solid, 0.15 g (13%), mp 150 °C (dec) (aqueous ethanol). Anal. calcd for C<sub>6</sub>N<sub>4</sub>O<sub>8</sub>K<sub>2</sub> • 1.5 H<sub>2</sub>O: C, 19.94; H, 0.83; N, 15.51. Found: C, 19.82; H, 0.71; N, 15.96..

*syn*-(Dimethoxyphosphinylmethyl,methyl)bimane 18. A mixture of *syn*-(bromomethyl,methyl)bimane 17 (7.0 g, 0.2 mol) and trimethyl phosphite (10 mL) was heated at 115 °C for 30 m as it became homogeneous and solidified. After trituration with hexane (50 mL) the mixture was taken up in ethyl acetate. The bimane 18 separated as a yellow crystalline solid, 6.3 g (78%); mp 224–225 °C; H NMR (CDCl<sub>3</sub>):  $\delta$  1.87 (d, 6 H, J = 4 Hz, CH<sub>3</sub>), 3.72

(d, 4 H,  $J = 22$  Hz,  $\text{CH}_2$ ), 3.75 (d, 6 H,  $J = 10$  Hz,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  159.52 (CO), 140.40 and 139.95 ( $\text{O}=\text{CC}=\underline{\text{C}}$ ), 114.91 and 114.58 ( $\text{O}=\text{C}-\underline{\text{C}}$ ), 53.52 and 53.19 ( $\text{PO}-\text{CH}_3$ ), 26.34 and 20.09 ( $\text{CH}_2$ ), and 6.83 ( $\text{CH}_3$ ); UV ( $\text{CH}_3\text{CN}$ ):  $\lambda$  ( $\epsilon$ ) 380 (6984); fluorescence (dioxane):  $\lambda$  ( $\Phi$ ) 417 (0.7); EI-MS: 408 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_8\text{P}_2$ : C, 41.17; H, 5.39; N, 6.86; P, 15.19. Found: C, 40.95; H, 5.35; N, 6.80; P, 15.41.

syn-(styryl,methyl)bimane 19. A mixture of the diphosphonate 18 (1.0 g, 2.5 mmol), potassium carbonate (1.4 g, 10 mmol), benzaldehyde (0.5 g, 5 mmol), and water (2 mL) was heated at  $100^\circ\text{C}$  for four h, cooled, combined with dichloromethane (200 mL), and washed with water (2 X 50 mL). The organic layer was dried (sodium sulfate) and concentrated to leave a brown solid that recrystallized from methanol to give the bimane 19 as a yellow crystalline solid, 0.3 g (29%); mp  $214-215^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  2.1 (s, 6 H,  $\text{CH}_3$ ), 7.3–7.8 (m, 14 H,  $\text{C}_6\text{H}_5\text{CH}=\text{CH}$ );  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  161.36 (CO); 149.92 ( $\text{O}=\text{C}-\underline{\text{C}}=\underline{\text{C}}$ ); 140.68 ( $\text{C}_6\text{H}_5\underline{\text{C}}=\text{C}$ ), 114.67 and 112.50 ( $\text{C}_6\text{H}_5\text{C}=\underline{\text{C}}-\underline{\text{C}}=\underline{\text{C}}-\text{O}$ ); 135.09, 129.68, 128.72, and 127.42 ( $\text{C}_6\text{H}_5$ ); 8.02 ( $\text{CH}_3$ ); UV ( $\text{CH}_3\text{CN}$ ):  $\lambda$  ( $\epsilon$ ) 400 (2530); fluorescence (dioxane):  $\lambda$  ( $\Phi$ ) 428 (0.2); EI-MS: 368 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2$ : C, 78.24; H, 5.47; N, 7.60. Found: C, 78.01; H, 5.52; N, 7.53.

To a slurry of potassium *t*-butoxide (0.8 g, 7.8 mmol) in *N,N*-dimethylformamide (DMF) (100 mL) the diphosphonate 18 (1.0 g, 2.5 mmol) in DMF (25 mL) was added with stirring under nitrogen at  $25^\circ\text{C}$  over a period of two h, heated at  $70^\circ\text{C}$  for three h, cooled, and treated with saturated aqueous ammonium chloride (10 mL). DMF was removed by distillation. The residue was treated with dichloromethane (200 mL), washed with water (2 X 50 mL), dried (sodium sulfate), and concentrated to give a brown solid that afforded the bimane 19 as a yellow crystalline solid, 0.22 g (25%), mp  $214-215^\circ\text{C}$ , after purification from methanol.

syn-(Acryloxymethylene,methyl)bimane 21. Triethylamine (3.6 g, 36 mmol) and acryloyl chloride (3.4 g, 36 mmol) were added separately to *syn*-(hydroxymethyl,methyl)bimane 20 (2.0 g, 9 mmol) in DMF (50 mL) with stirring at  $25^\circ\text{C}$  over a period of 48 h. The mixture was combined with water (200 mL), extracted with chloroform (3 X 100 mL), washed wi-



th aqueous sodium bicarbonate (5%) (30 mL), dried (sodium sulfate) and concentrated to leave a dark brown solid. Purification by flash chromatographic separation from a column of silica gel (80 g, chloroform) gave the bimane 21 as a yellow solid, 0.65 g (22%); mp 121-122 °C; H NMR (CDCl<sub>3</sub>):  $\delta$  1.9 (s, 6 H, CH<sub>3</sub>), 5.2 (s, 4 H, OCH<sub>2</sub>), and 5.8 – 6.6 (m, 6 H, CH<sub>2</sub>=CH); UV (CH<sub>3</sub>CN):  $\lambda(\epsilon)$  385 (7552); fluorescence (dioxane):  $\lambda(\Phi)$  432 (0.6); EI-MS: 332 (M<sup>+</sup>). Anal. calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>: C, 57.83; H, 4.81; N, 8.43. Found: C, 57.38; H, 4.79; N, 8.07.

syn-(Acetoxymethyl,methyl)(methyl,methyl)bimane 47. Bromine (1.25 g, 7.8 mmol) in dichloromethane (25 mL) was added dropwise to syn-(methyl,methyl)bimane (1.5 g, 7.8 mmol) in dichloromethane (50 mL) at 25 °C over a period of an hour. The solution was stirred for 30 min, and the solvent was removed to leave a red residue that was dissolved in dichloromethane (40 mL). The solution was mixed with aqueous potassium acetate (2 M, 30 mL) that contained cetyltrimethylammonium bromide (300 mg) and stirred for 18 hrs in the dark. The organic layer was separated, washed with water, and dried (anhydrous sodium sulfate). The solvent was then removed, and the yellow residue gave 0.78 g (40%) of syn-(acetoxymethyl,methyl)(methyl,methyl)bimane as a yellow crystalline solid: mp 185–186.5 °C (ethyl acetate); H NMR (CDCl<sub>3</sub>)  $\delta$  1.82 (s, 3 H, CH<sub>3</sub>), 1.94 (s, 3 H, CH<sub>3</sub>), 2.14 (s, 3 H, CH<sub>3</sub>), 2.33 (s, 3 H, CH<sub>3</sub>), 5.04 (s, 2 H, CH<sub>2</sub>); UV (dioxane):  $\lambda(\epsilon)$  373 (6836). Anal. calcd for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.31; H, 5.63; N, 11.38.

$\mu$ -Aminoimino-syn(methylene,methyl)bimane 24. Hydrazine hydrate (0.5g, 10 mmol) in acetonitrile (10 mL) was added to a solution of syn-(bromomethyl,methyl)bimane 17 (0.7 g, 2 mmol) in acetonitrile (25 mL) with stirring at 25 °C. The reaction mixture contained a colorless precipitate after 10 m that was collected by filtration after the mixture was diluted with water. The precipitate was triturated with acetonitrile, dried, and recrystallized from DMF to give the hydrazine 24 as a yellow solid, 0.3 g (68%); mp 220–221 °C (dec); H NMR (trifluoroacetic acid):  $\delta$  1.8 (s, 6 H, CH<sub>3</sub>), 4.5 (s, 4 H, CH<sub>2</sub>); <sup>13</sup>C NMR(trifluoroacetic acid):  $\delta$  165.70 (CO), 148.50 (O=CC=C), 116.6 (O=C-C=C), 48.3 (CH<sub>2</sub>), 5.4 (CH<sub>3</sub>); UV (CH<sub>3</sub>CN):  $\lambda(\epsilon)$  335 (57); fluorescence(dioxane):  $\lambda(\Phi)$  419 (0.1); EI-MS: 220 (M<sup>+</sup>).

Anal. calcd for  $C_{10}H_{12}N_4O_2$ : C, 54.54; H, 5.45, N, 25.45. Found: C, 54.33; H, 5.48; N, 25.33. The monoperchlorate derivative was prepared in ethanol as a yellow solid, 85%, mp 182–183 °C (dec);  $^1H$  NMR ( $D_2O$ ):  $\delta$  1.8 (s, 6 H,  $CH_3$ ), 4.03 (s, 4 H,  $CH_2$ ); UV ( $H_2O$ ):  $\lambda$  ( $\epsilon$ ) 339 (4611); fluorescence (water):  $\lambda$  ( $\Phi$ ) 460 (0.1); EI-MS: 220 ( $M^+ - HClO_4$ ). Anal. calcd for  $C_{10}H_{13}N_4O_6Cl \cdot 1.5 H_2O$ : C, 34.53; H, 3.74; N, 16.14; Cl, 10.21. Found: C, 34.59; H, 4.28; N, 16.28; Cl, 10.41.

The hydrazine 24 combined with acetone to give the hydrazone 25 (85%); mp 182–183 °C;  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.8 (s, 6 H,  $CH_3$ ), 2.0 [d, 6 H,  $C(CH_3)_2$ ], 3.8 (s, 4 H,  $CH_2$ ); UV ( $CH_3CN$ ):  $\lambda$  ( $\epsilon$ ) 339 (6932); fluorescence (dioxane):  $\lambda$  ( $\Phi$ ): 420 (0.15); EI-MS: 260 ( $M^+$ ). Anal. calcd for  $C_{13}H_{16}N_4O_2$ : C, 60.00; H, 6.15; N, 21.53. Found: C, 59.85; H, 6.09; N, 21.46.

N-Trifluoroacetyl  $\mu$ -amino-*syn*-(methylene,methyl)bimane 55. A suspension of  $\mu$ -amino-*syn*-(methylene,methyl)bimane 53 (0.50 g, 2.4 mmol) in trifluoroacetic anhydride (7 mL) was stirred at 25 °C for 2 h as a pale yellow precipitate appeared. The solvent was removed and the yellow residue recrystallized from a mixture of ethyl acetate and acetonitrile (1:1, 10 mL) to give the amide 55 as a colorless crystalline solid (0.30 g, 42%): mp 173–174 °C;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.86 (s, 3 H,  $CH_3$ ), 4.78 (s, 2 H,  $CH_2$ ); UV ( $CH_3CN$ ): 331 nm ( $\epsilon$  6309); fluorescence (dioxane):  $\lambda$  ( $\Phi$ ) 418 (0.8); EI-MS: 301 ( $M^+$ ). Anal. calcd for  $C_{12}H_{10}N_3O_3F_3$ : C, 47.85; H, 3.35; N, 13.95; F, 18.92. Found: C, 47.74; H, 3.34; N, 13.89; F, 18.73.

*syn*-Benzobimane 28. A solution of *syn*-(tetramethylene)bimane 26 (1.2 g, 5.0 mmol) in dioxane (50 mL) was treated with DDQ (2.3 g, 10.0 mmol). The solution was heated at 100 °C for twenty four hours as the reaction was monitored with thin layer chromatography (dichloromethane). After cooling a yellow precipitate was removed by filtration and the solvent was concentrated to give a dark brown residue which was redissolved in a minimal amount of dichloromethane and purified by chromatography (silica gel column, dichloromethane). The first fraction contained *syn*-(benzo)bimane 28 as a yellow solid (0.25 g, 29%), mp 308–310 °C;  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.3–8.0 (m); UV ( $CH_3CN$ ):  $\lambda$  ( $\epsilon$ ) 420 (6910);

fluorescence (50% aqueous ethanol):  $\lambda$  ( $\Phi$ ) 428 (0.9) (reference quinane sulfate  $\Phi$  0.55) [27]; EI-MS: 236 ( $M^+$ ). Anal. calcd for  $C_{14}H_8N_2O_2$ : C, 71.18; H, 3.41; N, 11.86. Found: C, 71.11; H, 3.41; N, 11.79. The following fraction contained *syn*-(benzo)(tetramethylene)-bimane 27 (0.51 g, 58 %) as a yellow solid, mp 226–227 °C;  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.88 (m, 4 H), 2.32 (m, 2 H), 2.80 (m, 2 H), 7.10–7.90 (m, 4 H); UV ( $CH_3CN$ ):  $\lambda$  ( $\epsilon$ ) 390 (8400); fluorescence (dioxane):  $\lambda$  ( $\Phi$ ) 435 (0.4); EI-MS: 240 ( $M^+$ ). Anal. calcd for  $C_{14}H_{12}N_2O_2$ : C, 69.99; H, 5.03; N, 11.66. Found: C, 69.87; H, 4.92; N, 11.56. *syn*-(Tetramethylene)-bimane 26 (0.30 g) was recovered in the final fraction. When five equivalents of DDQ were employed all of the starting material was converted; *syn*-(benzo)bimane 28 (0.85 g, 72%) was obtained and only a trace amount of *syn*-(benzo)(tetramethylene)bimane 27 was detected by thin layer chromatography.

4,6-Dibromo-1,2,3,4,6,7,8,9-octahydro-10H,12H-indazolo[1,2-*a*]indazol-10,12-dione 29. A solution of bromine (1.6 g, 10.0 mmol) in dichloromethane (20 mL) was added dropwise in the dark to a solution of *syn*-(tetramethylene)bimane 26 (1.2 g, 5.0 mmol) in dichloromethane (30 mL). The reaction was stirred for fifteen hours as a deep red solution gradually changed to orange. The solution was washed (aqueous sodium bicarbonate), dried (magnesium sulfate), concentrated, and the residue recrystallized from acetonitrile to give the dibromoindazoloindazoldione 29 as a yellow crystalline solid, 1.85 g (92%); mp 142–143 °C;  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.85–2.67 (m, 12 H), 5.57 (m, 2 H); EI-MS: 402 ( $M^+$ ). Anal. calcd for  $C_{14}H_{14}N_2O_2Br_2$ : C, 41.82; H, 3.51; N, 6.97; Br, 39.74. Found: C, 41.57; H, 3.43; N, 6.87; Br, 39.66.

DDQ (1.1 g, 5.0 mmol) and the indazoloindazoldione 29 (0.4 g, 1.0 mmol) were dissolved in dioxane (50 mL). The solution was heated at reflux for twenty four hours as the reaction was monitored with thin layer chromatography (dichloromethane) until the starting material 29 was consumed. *syn*-(Benzo)bimane 28, the major product, was detected by thin layer chromatography.

1,2,4,5-Tetrahydro-3H-benz[*g*]indazol-3-one 38. Hydrazine monohydrate (10.0 g, 0.2 mol) was added dropwise to a solution of ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate 37

(43.6 g, 0.2 mol) in methanol (100 mL). After an exothermic reaction subsided the solution was heated at reflux for two hours, and cooled to give a colorless precipitate that was isolated and recrystallized from hot methanol to give the indazolone 38, 23.2 g (62%), mp 214–215 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 2.70 (q, 4 H, CH<sub>2</sub>), 7.13–7.63 (m, 4 H, aromatic); EI-MS: 186 (M<sup>+</sup>). Anal. calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O: C, 70.95; H, 5.41; N, 15.03. Found: C, 70.70; H, 5.46; N, 15.14.

1*H*-Benz[*g*]indazol-3-ol 40. A sample of palladium (10% on charcoal) was added to a solution of the indazolone 38 in 1,2-dichlorobenzene (5 mL). The mixture was heated at reflux for two days as the reaction was monitored with thin-layer chromatography (dichloromethane). The catalyst was isolated, the solvent was removed, and an ivory solid residue was recrystallized from isopropanol to give the benzindazole 40, 0.39 g (78%), mp 245–247 °C (dec.); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 3.70. Anal. calcd for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.58; H, 4.40; N, 14.83.

3*a*-Chloro-2,3*a*,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one 39. Chlorine gas was slowly passed into a suspension of the indazolone 38 (20.0 g, 0.1 mol) in dichloromethane (250 mL) as the solid gradually dissolved. The yellow solution was stirred for thirty minutes and the solvent was removed to give a solid that recrystallized from a mixture of benzene and petroleum ether to give the chloroindazolone 39, 17.6 g (74%), 200–205 °C (dec); <sup>1</sup>H NMR (CDCl<sub>3</sub>-DMSO-*d*<sub>6</sub>): δ 2.30 (m, 2 H, CH<sub>2</sub>), 3.10 (m, 2 H, CH<sub>2</sub>), 7.20–7.90 (m, 4 H, aromatic), 11.72 (s, 1 H, NH). Anal. calcd for C<sub>11</sub>H<sub>9</sub>N<sub>2</sub>OCl: C, 59.88; H, 4.11; N, 12.70; Cl, 16.33. Found: C, 59.62; H, 4.08; N, 12.45; Cl, 16.07.

5,6,10,11-Tetrahydro-7*H*,9*H*-benz[6,7]indazolo[1,2-*a*]benz[*g*]indazol-7,9-dione 35. Potassium carbonate sesquihydrate (22.0 g, 0.13 mol) was added in one portion to a solution of the chloroindazolone 39 (11.0 g, 0.05 mol) in dichloromethane (100 mL). The mixture was stirred at room temperature as the reaction was monitored with thin-layer chromatography (dichloromethane). After the reaction was completed (16 h) the mixture was chromatographed (silica gel column, dichloromethane) to give an orange solid that was purified from a mixture of isopropanol and acetonitrile as the biman 35, 4.5 g (53%), mp 265–267 °C; <sup>1</sup>H

NMR ( $\text{CDCl}_3$ ):  $\delta$  2.58 (t, 4 H,  $\text{CH}_2$ ), 2.99 (t, 4 H,  $\text{CH}_2$ ), 7.03–7.38 (m, 8 H, aromatic); UV ( $\text{CH}_3\text{CN}$ ):  $\lambda$  ( $\epsilon$ ) 419 (3137); EI-MS: 340 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2$ : C, 77.63; H, 4.74; N, 8.27%. Found: C, 77.66; H, 4.83; N, 8.28%.

*syn*-( $\alpha$ -Naphtho)bimane 36. A sample of palladium (10 % on charcoal) (0.1 g) was added to a solution of the bimane 35 (3.4 g, 0.01 mol) in 1,2-dichlorobenzene (10 mL). The mixture was heated at reflux temperature for two days as the reaction was monitored with thin-layer chromatography (dichloromethane). Removal of the catalyst and solvent left a red residue that was purified from a mixture of hexafluoropropan-2-ol and methanol, as *syn*-( $\alpha$ -naphtho)bimane 36 as a yellow powder, 2.4 g (71%); mp 313–315 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.30–7.90 (m); UV ( $\text{CH}_3\text{CN}$ ):  $\lambda$  ( $\epsilon$ ) 460 (10,201); fluorescence ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda$  ( $\Phi$ ) 492 (0.1); EI-MS: 336 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{22}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 78.56; H, 3.60; N, 8.33. Found: C, 78.35; H, 3.66; N, 8.10. In the absence of a crystalline form an X-ray crystallographic analysis for the bimane 36 was not determined.

Acknowledgments. Financial assistance was received from ONR, ARO, Naval Weapons Center (China Lake, CA), and the Louisiana Board of Regents (LEQSF-RD-B-06). TGP<sup>c</sup> wishes to thank NOSC Independent Research program for support.

#### Footnotes and References

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Table 1  
*syn*-(A,B)Bimanes, Type I and *syn*(A,B)(A',B')Bimanes, Type II  
Laser Activity in the Region 500-530 nm

Compound (a,b)				Power Output,(mJ), P <sub>1</sub> and P <sub>2</sub>			
No.	A	B	Solvent(c)	P <sub>1</sub> (d)	RE (%)(e)	P <sub>2</sub> (f)	RE (%)(e)
<u>1</u>	CH <sub>3</sub>	CH <sub>3</sub>	HFI	2.45	41	5.27	43
<u>2</u>	CH <sub>3</sub>	Cl	TFE	1.75	29	5.15	42
<u>3</u>	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	H <sub>2</sub> O	4.37	72	10.92	89
<u>4</u>	FCH <sub>2</sub>	CH <sub>3</sub>	TFE(g)(h)	0.31	5	3.0	24
<u>18</u>	(CH <sub>3</sub> O) <sub>2</sub> P(O)CH <sub>2</sub>	CH <sub>3</sub>	H <sub>2</sub> O(i)	4.43	73	10.43	85
<u>20</u>	HOCH <sub>2</sub>	CH <sub>3</sub>	H <sub>2</sub> O	3.48	58	8.19	67
<hr/>							
	A,B	A'B'					
<u>26</u>	(CH <sub>2</sub> ) <sub>4</sub>	(CH <sub>2</sub> ) <sub>4</sub>	TFE(j)	0.70	12	2.60	21
<u>46(k)</u>	HOCH <sub>2</sub> ,CH <sub>3</sub>	CH <sub>3</sub> ,CH <sub>3</sub>	HFI(m)	0.23	4	2.39	19
<u>47</u>	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> ,CH <sub>3</sub>	CH <sub>3</sub> ,CH <sub>3</sub>	H <sub>2</sub> O(n)	0.7	15	4.98	56

(a) 10<sup>-3</sup>M. (b) Fluorescence in the region 435-460 nm with  $\Phi$  values in the range 0.6 to 0.9 was reported for compounds 1 [6], 2 [6], 3 [8], 4 [5c], 20 [8], 26 [6], and 46 [7]. See Experimental for compound 18. (c) HFI is hexafluoroisopropanol. TFE is trifluoroethanol. (d) Dye pumped to 5.0 J. (e) Relative efficiency compared to 100 (arbitrary) for coumarin 30. (f) Dye pumped to 10.0 J. (g) Mixed with water (10%). (h) Laser activity at 435 nm from bimane 4 in dioxane. (i) Laser activity at 438 nm from bimane 18 in dioxane. (j) Mixed with water (10%). (k) Rapid photodecomposition. (m) Concentration not determined. (n) 20% HFI.



Table 2  
 $\mu$ -X-syn-(Methylene, methyl)bimanes, Type III  
Laser Activity in the Region 500-530 nm

Compound (a,b)			Power Output (mJ), P <sub>1</sub> and P <sub>2</sub>			
No.	X	Solvent(c)	P <sub>1</sub> (d)	RE(%) (e)	P <sub>2</sub> (f)	RE(%) (e)
<u>5</u>	C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	HFI	4.76	79	10.00	82
<u>22</u> (h)	C(CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	TFE(g)	5.85	97	13.13	107
<u>24</u>	NNH <sub>2</sub>	H <sub>2</sub> O(i)	2.17	36	6.27	51
<u>50</u>	S	HFI	2.98	49	7.55	61
<u>52</u>	C(CN) <sub>2</sub>	H <sub>2</sub> O(j)	0.17	3	0.4	3
<u>53</u> '	NH	H <sub>2</sub> O	0	0	1.22	9
<u>55</u>	NCOCF <sub>3</sub>	TFE(g)	0.33	5	1.6	13

(a) 10<sup>-3</sup>M. (b) Fluorescence,  $\lambda$  ( $\Phi$ ): 426 (0.8) for compound 5 and 447 (0.8) for compound 50 were reported [7]. See Experimental for compounds 22, 24, and 55. (c) HFI is hexafluoroisopropanol. TFE is trifluoroethanol. (d) Dye pumped to 5.0 J. (e) Relative efficiency compared to 100 (arbitrary) for coumarin 30. (f) Dye pumped to 10.0 J. (g) Mixed with water (10%). (h) Ref 7. (i) Contained perchloric acid. An aqueous solution of the perchlorate salt (Experimental section) in water gave no laser activity when pumped to 5.0 J and 0.43 mJ (RE 3.5%) when pumped to 10.0 J. (j) Mixed with 20% HFI.

Figure 1. Absorption (S-S and T-T), fluorescence (FL) and the center of broadband laser activity at 438 nm for *syn*-(dimethoxyphosphinylmethyl,methyl)bimane 18 in *p*-dioxane. The T-T absorption spectrum was recorded at 77°K, employing a  $2 \times 10^{-4}$  molar solution of 2-methyltetrahydrofuran. The S-S and Fl ( $1 \times 10^{-3}$  molar) spectra were recorded with *p*-dioxane as solvent.

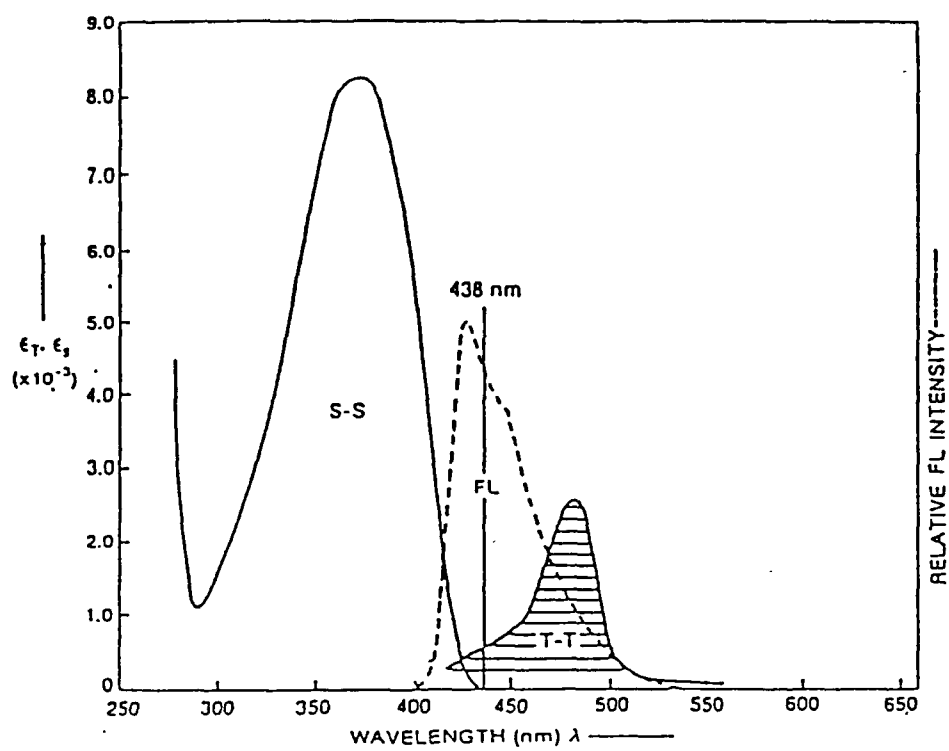


Figure 2. Absorption (S-S and T-T), fluorescence (FL), and the center of broadband laser activity at 514 nm for *syn*-(dimethoxyphosphinylmethyl,methyl)bimane 18. The T-T absorption spectrum was recorded at 77°K, employing a  $2 \times 10^{-4}$  molar solution of 2-methyltetrahydrofuran. The S-S and Fl ( $1 \times 10^{-3}$ ) spectra were recorded with water as a solvent.

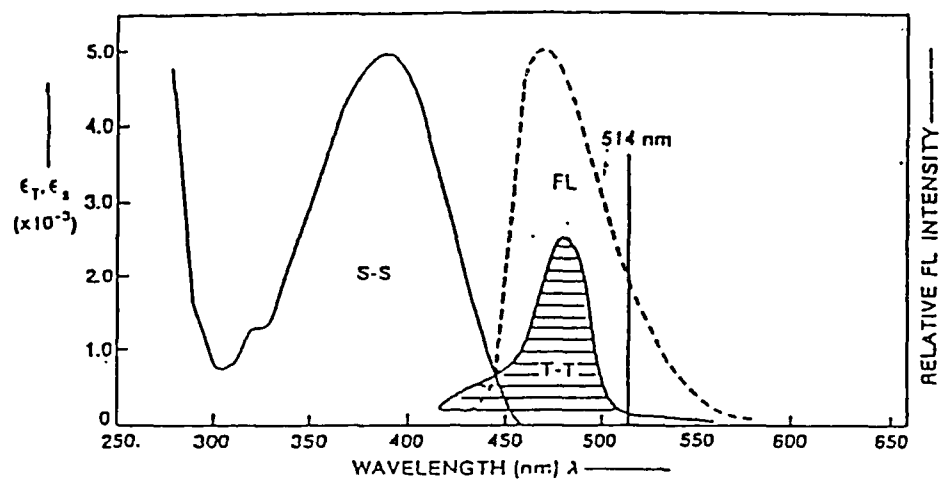
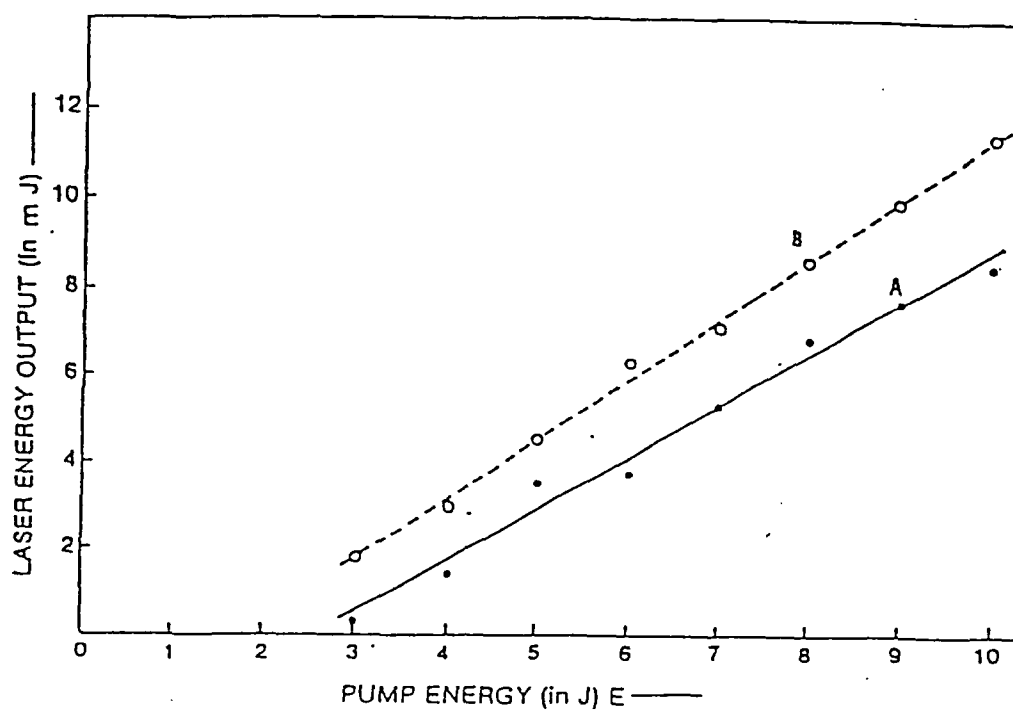


Figure 3. Laser energy output (mJ) as a function of flashlamp pump energy (J) of (A) *syn*-(dimethoxyphosphinylmethyl,methyl)bimane 18,  $1 \times 10^{-3}$  molar in water and (B) coumarin 30,  $7.5 \times 10^{-4}$  molar in ethanol.



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